Conductive Metal-Organic Frameworks and Networks: Fact or Fantasy?

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PCCP Invited Perspective

Abstract

Electrical conduction is well understood in materials formed from inorganic or organic building blocks, but their combination to produce conductive hybrid frameworks and networks is an emerging and rapidly developing field of research. Self-assembling organic-inorganic compounds offer immense potential for functionalising material properties for a wide scope of applications including solar cells, light emitters, gas sensors and bipolar transparent conductors. The flexibility of combining two distinct material classes into a single solid-state system provides an almost infinite number of chemical and structural possibilities; however, there is currently no systematic approach established for designing new compositions and configurations with targeted electronic or optical properties. We review the current status in the field, in particular, the range of hybrid systems reported to date and the important role of materials modelling in the field. From theoretical arguments, the Mott insulator-to-metal transition should be possible in semiconducting metal-organic frameworks, but has yet to be observed. The question remains as to whether electro-active hybrid materials will evolve from chemical curiosities towards practical applications in the near term.

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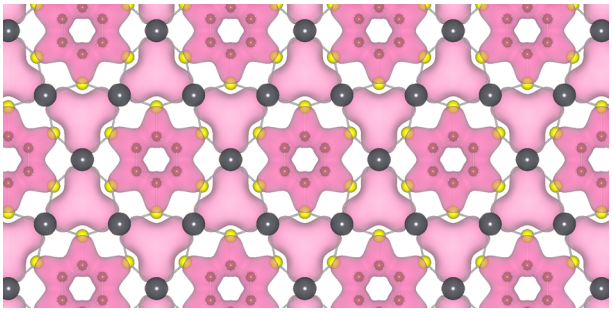
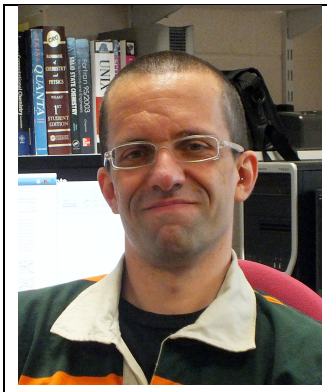


This perspective addresses progress in the understanding of conductive hybrid organic-inorganic materials.

Biographies

Christopher Hendon was born in Boulder, Colorado and moved to Melbourne, Australia, where received his BSc Adv. (2009) from Monash University, Australia. His honours (2010) work was studying the extent of proton transfer in protic ionic liquids, supervised by Dr. Katya Pas and Prof. Douglas MacFarlane. He is now on an international scholarship, studying towards a PhD in the University of Bath on the nano-architecture of metal-organic systems, using a combination of computational and synthetic chemistry.



Davide Tiana obtained his BSc and PhD at the University of Milan (2005). During his bachelor's degree he studied protein denaturation. His Masters and PhD projects were focused on the study of organo-metallic interactions. After completing his PhD (2010) in computational and theoretical chemistry, he spent one year at the University of Augsburg analysing hydrogen activation in silane compounds. In 2012 he moved to the University of Bath as a postdoctoral associate where he works on electrical, magnetic and superconducting properties of coordination polymers.

Aron Walsh received his BAmod (2003) and PhD (2006) in chemistry from Trinity College Dublin. He worked at the National Renewable Energy Laboratory (USA) as a postdoctoral associate, and then at University College London as a Marie Curie Fellow. In 2011 he joined the Department of Chemistry at the University of Bath, where his research group, in the Centre for Sustainable Chemical Technologies, focuses on the development and application of computational techniques for functional materials design and characterisation. His research is supported by the Royal Society, EPSRC, and the European Research Council.

Introduction

As devices continue to shrink in dimension and simultaneously require greater efficiencies, controlled electronic structure engineering at the nanoscale presents new difficulties. In place of traditional extrinsic doping approaches, it is more desirable to functionalise the materials *themselves*. Self-assembling hybrid organic-inorganic networks offer immense potential for tailoring material properties for a wide scope of technological applications including low-cost solar cells, solid-state lighting, gas sensors, and bipolar transparent conductors. Initial experimental success in this area has demonstrated the viability of these materials and has attracted significant interest in this rapidly growing field of research.[1, 2]

Materials chemists generally focus on inorganic or organic systems. Their combination to produce hybrid materials is an area that has emerged from the first coordination polymers (CPs) developed in the early 20th century to a family of systems that has been exponentially expanding over the past decade, spanning from 1D CPs to 3D metal-organic frameworks (MOFs), and encompassing the 2D metal-organic networks present in organic and hybrid optoelectronic devices. Much progress has been made in the synthesis and characterisation of novel materials, with a rich variety of chemical and physical properties including record surface areas of up to 10000 m^2g^{-1},[3] negative thermal expansion,[4, 5] reversible "breathing" phase transitions,[6] ferroelectricity,[7, 8] and ferromagnetism.[9]

The construction of hybrid materials offers an almost infinite number of chemical and structural possibilities. The structural diversity of these systems has been discussed by Cheetham, Rao and Feller,[10] who introduced a systematic notation, I^mO^n, based on the dimensionality of the underlying inorganic (I^m) and organic (O^n) frameworks. There have been a number of recent reviews on the topic, for instance Natarajan and Mandal addressed porous transitional-metal frameworks with a particular emphasis on magnetic properties,[11] while Rao, Cheetham and Thirumurgan addressed the solid-state physics of hybrid materials including dielectric and optical properties.[12]

Computer simulation techniques, including electronic structure and atomistic simulation methods, have played an important role in the structure prediction of framework materials as reviewed by Mellot-Draznieks[13] and Catlow and Woodley.[14] For gas storage applications, a simple figure of merit for material performance is the accessible surface area, which has recently been targeted by a large-scale computational

screening including both known and hypothetical porous MOF-5,[15] and is matched by a large effort for high-throughput experimental synthesis.[16] The chemistry of metal oxide – polymer interfaces for organic photovoltaics has been led by pioneering simulations from the group of Bredas.[17]

The focus of this Perspective is hybrid materials than can conduct electricity, thus opening up a new area for applications for these materials. *Is it possible to combine the high conductivity and crystallinity of inorganic semiconductors with the flexibility and facile synthesis of organic semiconductors?* There have been a large number of reports of "semiconducting" frameworks over the past few years; although, in many cases this assignment has been made on the basis of the magnitude of the optical band gap alone, which is only tangentially related to the stability and transport of electron and hole carriers. We succinctly review the essential physics and chemistry of inorganic and organic semiconductors, before assessing the variety of semiconducting or potentially semiconducting hybrid materials that have been synthesised and characterised. Finally, we address the fundamental physical limitations, research challenges, and future outlook of these systems.

Inorganic Semiconductors

Inorganic semiconductors are at the heart of the modern electronics industry, but also in the developing field of solar energy harvesting. When a material with a finite separation between its valence (filled) and conduction (empty) bands absorbs a photon of light with sufficient energy, an electron and hole are created in the system. The conversion of this electronic energy to an external electrical voltage, or to facilitate a redox reaction, is the goal of all photovoltaic and photoelectrochemical devices.[18] An example of this process is shown in Figure 1.

In addition to the creation of electron or hole carriers in materials, long carrier lifetimes and high carrier mobility are of crucial importance for device applications. There are three primary classes of inorganic compounds that fulfill these criteria: group 14 elemental semiconductors (*e.g.* Si, Ge and Sn); II-VI semiconductors (*e.g.* ZnO, CdS, MgTe) and III-V semiconductors (*e.g.* AlN, GaP and InAs). Of course more complex multi-component materials and their alloys can also be formed.[19-21] For high-quality inorganic materials, the mobility (μ) of electrical carriers can vary from 150 $cm^2V^{-1}s^{-1}$ in ZnO to 7 $\times 10^4$ $cm^2V^{-1}s^{-1}$ in InSb, with typical carrier concentrations ranging from 10^{16} to 10^{21} cm^{-}

[3,22] Corresponding values of conductivity range from 10^{-9} Scm^{-1} in ultra-pure ZnO, to 2×10^3 Scm^{-1} in highly doped samples. These electrically active charge carriers can be created by the formation of point defects in the lattice, through deliberate doping of aliovalent impurities, or by thermal or photo-excitation.[23, 24]

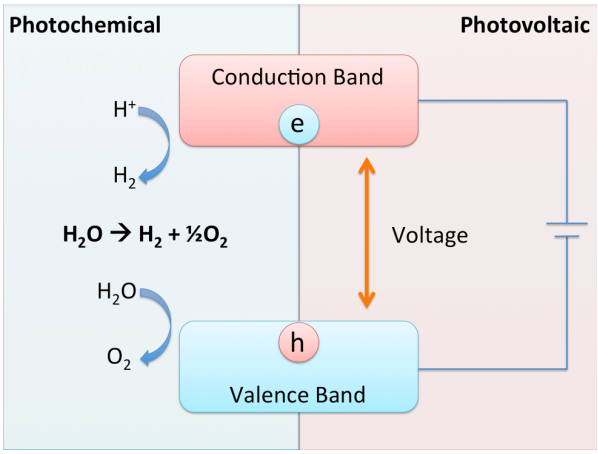


Figure 1 Schematic of how an excited state (electron e^- and hole h^+) in a semiconducting material can be used to produce electrical energy in a solar cell, or chemical energy in a photochemical cell.

There is an important distinction between intrinsic semiconducting materials with small band gaps, where thermal energy is sufficient to create significant concentrations of electron and hole carriers, and wide band gap semiconductors, where defects and/or doping is required in order to increase the carrier concentrations and hence reduce the electrical resistivity. While the physics of intrinsic semiconductors is well understood,[25] the behaviour of wide band gap materials is still a matter of debate from both experimental and theoretical viewpoints. For example, the origin and control of conductivity in ZnO has produced an immense amount of literature, with only limited quantitative progress.[24, 26-31]

For inorganic materials, the most common mode of conduction can be understood from the fundamentals of band theory, where electrical carriers are considered to move through delocalized bands and can be assigned an effective mass (m*) that is related to the curvature of the electronic band structure in reciprocal space. However, there is also the possibility for the formation of electron or hole states localized on the lattice. Trapped polaronic states typically form in inorganic materials where the effective mass is large, such as transition metal oxides ($m^* > 1$); chemically this can be interpreted

simply as a change in the oxidation state of the anion (hole polarons) or cation (electron polarons).[32]

It is now well understood that inorganic materials can exhibit a non-metallic (localized electrons) to metallic (delocalized electrons) transition once a critical carrier concentration is reached, where the wavefunctions of the conduction electrons begin to overlap. This transition, originally discovered by Mott[33] and later refined by Edwards and Seinko,[34] can be quantified by the Mott criterion: $n_e^{1/3} a_H = 0.26$, where n_e is the critical carrier concentration and a_H is the effective electron radius, which is inversely proportional to m*. This is a universal phenomenon in inorganic semiconductors that has been validated for materials ranging from Si to WSe_2 to In_2O_3.[34, 35] Therefore, once sufficient curvature in the band structure is present, in principle, high levels of conductivity can be achieved by control of the level of doping.

Organic Semiconductors

Organic semiconductors exhibit a rich variety of properties and forms, ranging from molecular conductors and charge-transfer salts to chains of polymeric materials. It is difficult to generalise their chemical and physical behaviour, but we can make some pertinent observations.

Conductivity in organic materials is closely related to aromaticity, where conjugation of π bonds can facilitate efficient transport of electrons. The majority of these materials are of *p*-type character, corresponding to mobile holes in the π framework, which is a reversal of the preference of most inorganic systems that favour *n*-type conduction. Pentacene is considered the benchmark organic semiconductor with a hole mobility as high as 35 $cm^2V^{-1}s^{-1}$ at room temperature.[36] Following the development of "molecular metals" based on donor-acceptor architectures such as tetrathiafulvalene – tetracyanoquinodimethane (TTF-TCNQ),[37] one recent success in the electronic structure engineering of organic molecular conductors is the demonstration that an asymmetric molecule (naphthalene diimide) can itself act as a molecular *p-n* junction, due to the spatial separation of electron and hole wavefunctions.[38]

The most dramatic microscopic change between inorganic and organic semiconductors is that the latter are predominately structurally disordered. The structural inhomogeneity and low dielectric screening favour the localization of electron and hole carriers: the formation of small polarons, or in the context of

amorphous semiconductors, Anderson localization. Carriers can be rapidly trapped at the femto-second time-scale, and the fundamental implication of localized carriers is that electron transport becomes thermally activated through carrier hopping or tunneling.[39] This phenomenon is common to both molecular organic crystals and extended polymers. However, it is possible to extrinsically dope these materials to high carrier concentrations beyond the Mott criterion discussed in the previous section. For example, Li metal doping of picene was recently shown to undergo a semiconductor to metal transition, with a further superconductor transition observed at low temperatures.[40]

While it is now possible to grow high-quality single crystal films of molecular organic crystals, as the molecular building blocks are bound largely through van der Waals interactions, structural disorder in the form of dislocations and grain boundaries is common. Although the effect of microstructure is less critical than for inorganic semiconductors, these extended defects still act as a barrier for electron transport.[41] Furthermore, as a result of preferential stacking directions, organic crystals usually exhibit highly anisotropic physical properties (*e.g*. orientation dependent ionization potentials).[42]

One common feature of both organic and inorganic semiconductors is the role of charged point defects in generating the electron and hole carriers responsible for conduction. For example, even undoped π-conjugated polymers have been shown to have carrier concentrations up to 10^{17} cm^{-3}, orders of magnitude larger than the ideal intrinsic value of 10^{5} cm^{-3} based on the magnitude of the band gap and available thermal energy, which is believed to arise from a combination of site vacancies, interstitials and substitutions.[43] The conductivity of highly doped organic semiconductors can exceed 100 Scm^{-1} at room temperature, which approaches the performance of their inorganic counterparts.

Hybrid Frameworks

While the physico-chemistry of inorganic and organic semiconductors themselves is rich in complexity and diversity, hybrid semiconductors that combine building blocks from both regimes represent a new paradigm. These materials are not yet fully understood or controllable, but what is known thus far?

Metal-Organic Polymers

One-dimensional metal-organic polymers (I^0O^1) are the simplest and the "least" structurally complex class of hybrid materials. A range of possible topologies is shown in Figure 2. Despite their apparent simplicity, a poor understanding of the role played by initial experimental conditions make the synthesis and the characterization of 1D CPs a significant challenge.[44] Indeed, although Bailar[45] wrote the first review of the field in 1964, there were only 511 publications related to metal-organic polymers up to 1993.[46] Thanks to the improvements in X-ray crystallographic techniques and in the understanding of the growth process,[47] the situation has changed over the last fifteen years with more than 5800 publications up to 2011.[48]

Due to their restricted dimensionality, CPs are an ideal benchmark system to study and to understand the non-covalent interactions that underlie hybrid materials. In addition, CPs can be used in the development of magnetic, non-linear optical and conductive materials with higher dimensionality (i.e. I^0O^1 and I^0O^2 compounds), as recent reviewed by Givaja *et al.*[49] The rest of this section will be focused on explaining how and why these polymers exhibit electrical activity, which will be illustrated with a small number of examples. Readers interested in the detailed topologies or in more general features and properties can refer to previous reviews.[44, 48, 50]

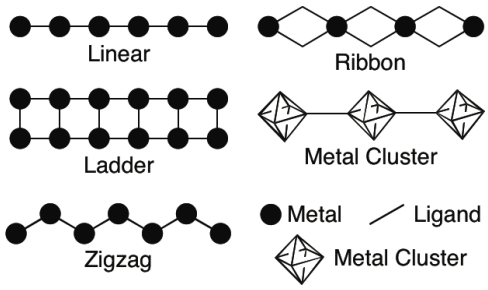


Figure 2 Representations of common 1D coordination polymers topologies. Adapted from Ref [48].

Electrical conductivity of polymers continues to be one of the most important research areas for materials science. The first studies on "synthetic metals" started in the late 1970s with the synthesis of polyacetylene. This discovery had such a major impact on the society that Heeger, MacDiarmid and Shirakawa, were awarded the chemistry Nobel Prize in 2000.[51-53] As explained above, conductivity in organic polymers is possible thanks to the conjugation of π bonds. Concerning the CPs, they can exhibit electrical

conductivity through the overlap of the ligand π^* and the metal d_π orbitals. Indeed, electron transfer between two metal centres can occur across bridging ligands. Through a targeted selection of metals and ligands, the band gap and conductivity can be modulated, making the construction of hybrid materials with metallic, semi-conducting and insulating behaviour tuneable.

Donor-acceptor complexes are amongst the most studied hybrid compounds with conducting properties. The prototype of such charge transfer compounds can be considered the organic complex between the electron donor TTF and the electron acceptor TCNQ shown in Figure 3.[54-57] This molecule shows a metallic behaviour above 60K with a maximum of conductivity of σ = 1.5 × 10^4 Scm^{-1}. Below that temperature, due to a Peierls distortion, a transition to semi-conducting state occurs.[58]

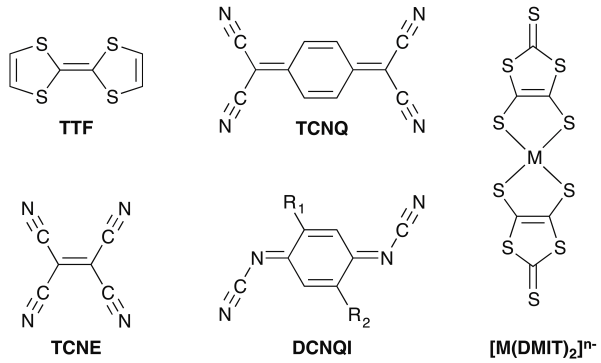


Figure 3 Molecular structures of (TTF), 7,7,8,8-tetracyanoquinodimethane (TCNQ), tetracyanoethylene (TCNE), N,N'-dicyanoquinoedimine (DCNQI), M-4,5-dimercapto-1,3-dithiol-2-thione ($M(DMIT)_2$) with M=Ni,Pd,Pt. Charge-transfer salts such as [TTF][TCNQ] crystalize with stacks of donors (D) and acceptors (A): DADADA.

Regarding hybrid materials, in 1986, Bousseau *et al.* synthesised a novel class of CPs combining TTF with $M(dmit)_2$.[59] Noteworthy is that, while nickel and palladium compounds have metallic behaviour at room temperature ($\sigma \sim$ 300 Scm^{-1} and $\sigma \sim$ 750 Scm^{-1} for Ni and Pd, respectively), the platinum material is a semiconductor ($\sigma \sim$ 20 Scm^{-1}). Furthermore, TTF-$[Ni(dmit)_2]$, unlike common "1D metal" compounds, exhibits metal-like conductivity down to at least 4K with an increase of conductivity up to $\sigma \sim$ 1.5 x 10^5 Scm^{-1}. This can be explained observing that S-S inter-stack interactions occur amongst peripheral sulphur atoms. This gives rise to a 2D network that avoids the instability associated with the Peierls transition (Figure 4).[58]

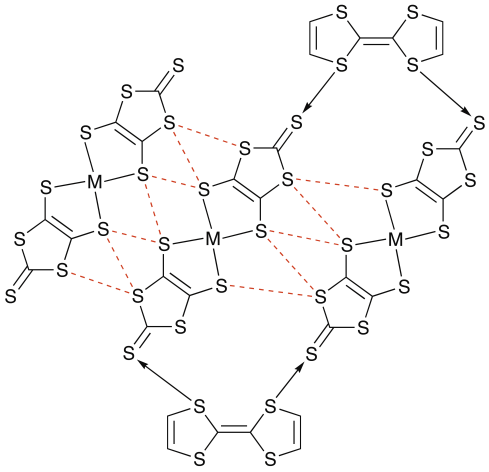


Figure 4 An illustration of the charge transfer (black arrow) between TTF and $M(dmit)_2$ and the peripheral contacts between S atoms (red dashed line). Such van der Waals interactions yield a 2D network that avoids the instability associated with the Peierls transition. Adapted from Ref **59**.

Another type of charge transfer hybrid compound has been synthesised by Dunbar using organocyanide ligands such as TCNQ, DCNQI and TCNE (DCNQI = N,N'-dicyanoquinonediimine, TCNE = tetracyanoethilene), which show interesting conductive properties.[60-62] TCNQ can chelate metals as a tetra-dentate as well as bi-dentate ligand allowing the synthesis with both 1:1 and 1:2 M:TCNQ ratio. For instance, two polymorphs of Cu(TCNQ) as well as $Cu(TCNQ)_2$ have been reported in the literature.[59, 63] Although all of these compounds are semiconductors, the conductivity at room temperature varies from 0.25 Scm^{-1} to 1.3×10^{-5} Scm^{-1} for Cu(TCNQ) and 2×10^{-6} Scm^{-1} for $Cu(TCNQ)_2$. On the other hand, the coordination of Cu with DCNQI (*i.e.* $(DCNQI)_2Cu$) yields a "molecular metal" with σ increasing from c.a. 800 Scm^{-1} at room temperature to 5×10^5 Scm^{-1} at 3.5K.[64] This unusual charge-transport behaviour is due to the existence of an isotropic 3D conduction pathway in addition to the usual 1D pathway through stacks of DCNQI radicals.[65] The last common ligand used in charge transfer compounds is TCNE. A reductive coupling on the metal center yields the compounds shown in Figure 5,[66] which are of considerable interest in materials applications owing to their similarities to the metal phthalocyanine.

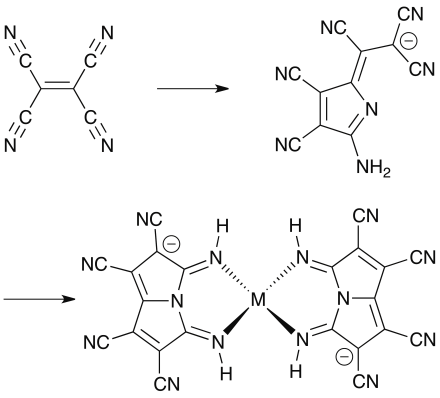


Figure 5 Schematic representation of TCNE reductive coupling reaction. The similarity of the product with phthalocyanine makes it interesting for conductive studies in CPs. Adapted from Ref [66].

One class of phthalocyanine-based conductive CP is shown in Figure 6.[67] It has been found that the conductivity can be improved using better π-bonding metals (Os > Ru > Fe) or increased π-ligand acidity (pyridine > bipyridine > 1,4-diazabicyclo[2,2,2]octane (dabco)).[68] Doping such compounds with iodine results in moderate levels of conductivity ranging from 1×10^{-6} to 2×10^{-1} Scm^{-1}.

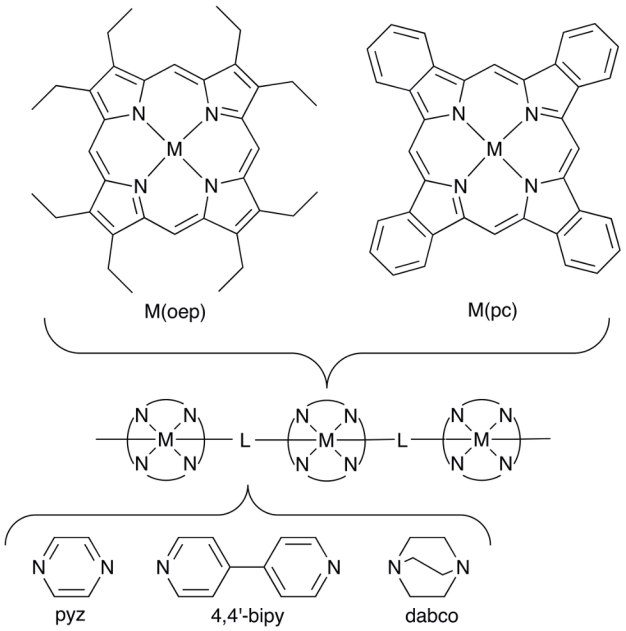


Figure 6 Representation of bridging 1D coordination polymers with conductive properties. M= Fe, Ru, Os. Conductivity increases going down into the group (*i.e.* Os > Ru > Fe) and using a stronger π acid ligand (*i.e.* pyz > bpy > dabco). Adapted from Ref [67].

It should be noted that, generally, Ru(II) and Os(II) complexes are good choices for assembling conductive coordination polymers. Indeed, these two transition metals have valence electrons that can be easily delocalized across the bridging ligands and, due to

their largely nonbonding character, the coordination sphere of the metal is not appreciably changed by one-electron oxidation. Hence, oxidative doping of polymers employing these elements should result in little structural change to the polymer backbone. The formation of trapping centres (polarons) that limit the carrier mobility is thus minimized.[69] Another class of phthalocyanine showing conductive properties can be found amongst compounds formed from group 10 metals (Ni, Pd, Pt). These metal complexes often stack in layers as shown in Figure 7. In these compounds, it is not the π^*-d_π orbitals overlapping that is responsible for conductivity, but instead a π-π orbital overlap present between the different layers. Indeed, an interlayer distance of around 3 Å is too long for a direct interaction between metal atoms, but is optimal for π-π stacking.[46] Oxidation of such materials usually promotes them from an insulating or semiconducting state to a metallic one. One notable case is $Ni(Pc)(I_3)_{0.33}$, where the conductivity increases from ~500 Scm^{-1} at room temperature to 5000 Scm^{-1} at 20 K.[47]

In other compounds, metal-metal contacts (*i.e.* direct overlap of the d_{z^2} metal orbitals) are responsible for the conductive properties, as for example in Ag polymeric complexes.[70-74] The Ag(I) ion has a $4d^{10}$ electronic configuration that exhibits a tendency to form metal-metal interactions, with an Ag-Ag distance below the sum of the van der Waals radii (*i.e.* 3.44 Å).[75] Ag is commonly employed in the preparation of new functional solids owing to its variety of coordination numbers, and also the potential Ag-Ag interaction. Taking advantage of such features, Lin *et al.* synthesized a series of Ag-cyanopyridine polymers with semiconducting properties.[72] Also noteworthy is the silver acetate synthesized by Olson *et al.* with an Ag-Ag distance of about 2.80 Å, shorter than the one present in Ag metal (2.89 Å).[76] The simultaneous presence of metal-metal and π-π interactions can lead to the formation of 2D networks, which will be discussed in the next section.[73, 77, 78]

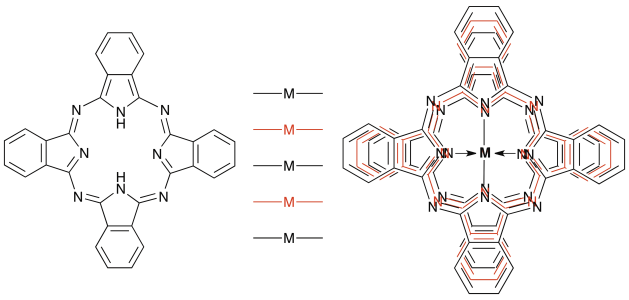


Figure 7 Phthalocyanine structure (left) can coordinate to a metal. These molecules usually stack in a column (right), originating from the aromatic quadrupole interactions. Such motifs yield conduction in CPs through π- π orbital overlap.

Having described the types of interactions involved between metals and organic ligands in CPs, some comments have to be made on the conductivity related to the CP ligand (*i.e.* the organic component). The classification of a material as an electron donor (*p*-type) or electron acceptor (*n*-type) is associated with to a low ionization potential (IP) or high electron affinity (EA), respectively.[79] In both cases the conductivity can be related to the mobility of carriers inside the conjugated system. While remarkable progress has been achieved in the development of *p*-type channels[80, 81], progress in the construction of robust *n*-type channels has not been successful. Indeed, despite the fact that the necessary criteria for designing *n*-type materials are well known (*i.e.* high EA, ordered structures),[82-86] the requirement of a high EA causes the synthesis of new materials to be quite difficult and makes such compounds unstable towards oxygen and moisture. This problem remains one of the major challenges in organic electronics.[87]

Concerning hybrid compounds, interesting results for electron conduction have been obtained using phthalocyanine[88, 89] and tetrathioterephtalate anions, with some examples shown in Figure 8. On the other hand, for strictly organic polymers, good results have been obtained with naphthalene and dicianomethylene quinoids.[90-92]

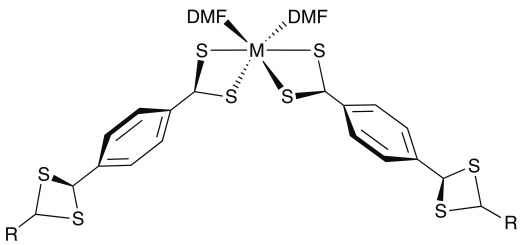


Figure 8 Structure of a metal tetrathioterephtalate. M= Zn,Mn. DMF=dimethylformamide.

At present, the most promising results in developing *n*-type substances with relatively high mobility, and stability in air, have been obtained using perylene derivatives.[87, 93] A mobility of $\mu = 1.7 \times 10^{-2}$ $cm^2V^{-1}s^{-1}$ has been reported for the case of the N,N'-bis(4-trifluoromethylbenzyl)perylene-3,4,9,10-tetracarboxilic diimide (PTCDI-TFB) as shown in Figure 9.[94]

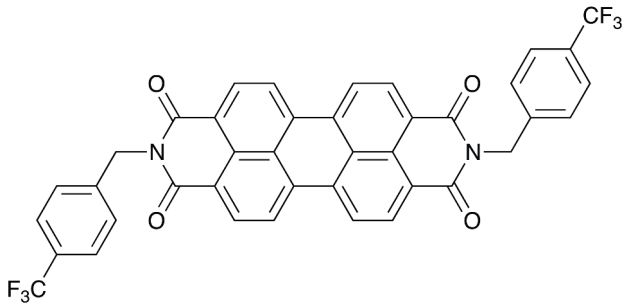


Figure 9 Structure of PTCDI-TFB. With a high carrier mobility, this kind of molecule represents one of the most promising *n*-type organic ligands.

The perylenediimide ligands are of particular interest not only because of their high EAs but also because of the fact that their electronic properties can be tuned in a rational way through synthetic manipulation of the substituents around the core.[87, 95] Finally, another interesting molecule that could form a good class of *n*-type compounds is difluorodioxocyclopentene-annelated terthiophene (molecule **A**, Figure 10).[86, 96] While these more exotic ligands have not yet been adapted into hybrid metal-organic compounds, it is likely that they will be targeted in the near future.

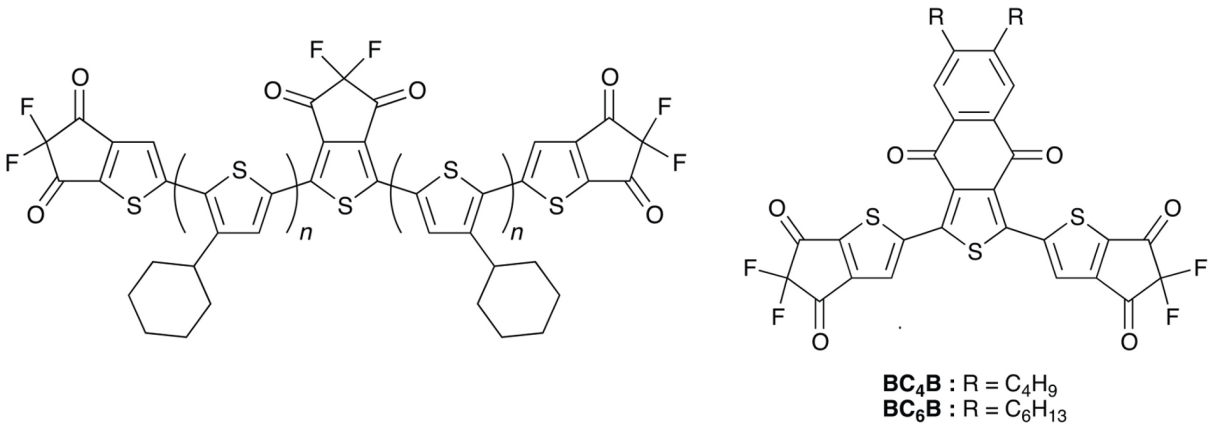


Figure 10 On the left, the original structure of **A** as synthesised by Umemoto *et al.*[96] On the right, the modified molecule synthesised by Ie *et al.*[86], which yield carrier mobilities of $\mu=1.6\times10^{-2}$ (**BC4B**) and $\mu=1.4\times10^{-2}$ $cm^2V^{-1}s^{-1}$ (**BC6B**), respectively.

Beyond 1D: Hybrid Networks and Quantum-well Structures

The logical extension of 1D CPs is to implement another direction of molecular connectivity. 2D hybrids (I^0O^2 and I^2O^0) have been shown to have applications as catalysts,[97, 98] photo-emitters[99-102] and of particular interest to this review, as potential light harvesting photovoltaic compounds.[103-106] The multitude of applications is the product of the various structural motifs that multidimensional hybrids are built upon.

These systems have graphite-like sheet characteristics, although they may not always be visually well defined. Hybrids are 'designer' materials and their composition is defined by both the metal ions and the organic ligands that hold them together. Copper, tin, lead and zinc are the most frequent metals used for forming I^1O^n and I^2O^n structures due to their regular geometric conformations (tetrahedral, octahedral and cubic), as well as previous literature precedent that these compounds form semiconducting oxides, iodides and sulfides.[22] Pb has attracted the most attention because of its highly tunable electronic properties. Several publications describe systems based specifically on iodoplumbates and within that group there are a multitude of connectivities and conformations.[107-111] Eight coordinate Pb has been shown to have potential for applications in solar cells,[112] whilst six coordinate lead is ubiquitous in the literature and seemingly a valuable starting point towards photo-active hybrid materials owing to the low band gaps associated with the compounds of Pb(II), and the interesting material physics associated with lead chalcogenide quantum dots.[113, 114]

The other half of these hybrid networks concerns the choice of ligand. Recent literature details examples where the ligand is not only structural but also a source of electronic excitation. Controlling properties based on ligand choice is still in its infancy and so there is much scope for future work in this area. There is very little information on how to control the effects on the system of these photoactive ligands. In addition to the ubiquitous aromatic moieties (terephthalic acetate, pyridine etc.), common organics include primary amines and carboxylates (aliphatic carboxylates, amines; substituted aromatics),[10, 97, 98, 115, 116] and the most fundamental single atom variants; pnictogens, chalcogenides and halides.[115, 117, 118]

Structural Motifs. Of the aforementioned metals, the cubic, octahedral and tetrahedral coordination geometries are dominant. Our ongoing research concerns the

cubic lead centered 3D hybrid, $Pb(C_6S_6)$ (depicted in Figure 11),[112] as well as other group-II metal variants.

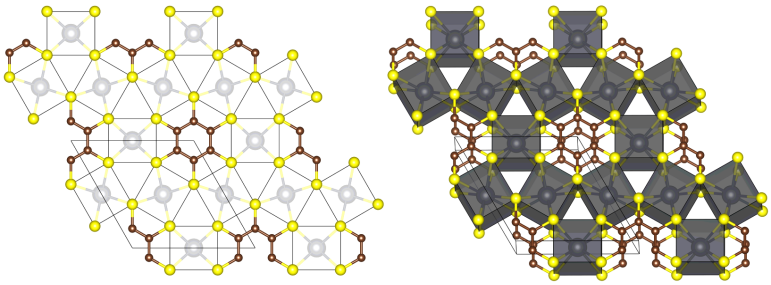


Figure 11 Hexagonal crystal structure of lead benzene hexathiolate, a 3D hybrid with 8 coordinate lead. The cubic Pb-centred polyhedra are shaded black, while the S atoms are coloured yellow.

Cubic coordination environments are exclusively observed for the larger metal ions, whose atomic radii are equal to, or larger than, that of Pb (1.75 Å).[119] As a result, Y is an interesting candidate for structural building blocks. Some reports have shown yttrium to take unusual three-coordinate motifs[120, 121] but, more importantly, it has been demonstrated to have eight-coordinate geometry, a similar atomic radii, and differing oxidation states to that of Pb.[122] In the work of Mishra *et al.* lead iodide is observed as six-coordinate, one of the more common conformations. Distorted octahedral geometries are observed with Pb, Sn and Bi,[123] and are best demonstrated 2D tin iodide in the perovskite geometry.[124-126] Tetrahedral geometries are most common for smaller metal ions like Cu(I/II), Zn(II) and occasionally Sn(II).[127-129]

There is no empirical evidence that suggests the geometry of the metal dictates the electronic trends. In fact the only clear conclusion from examining the metals themselves is that compounds based on large main group elements like Sn, Pb and Bi, have highly tunable properties, and range from metallic to insulating depending on ligand selection.

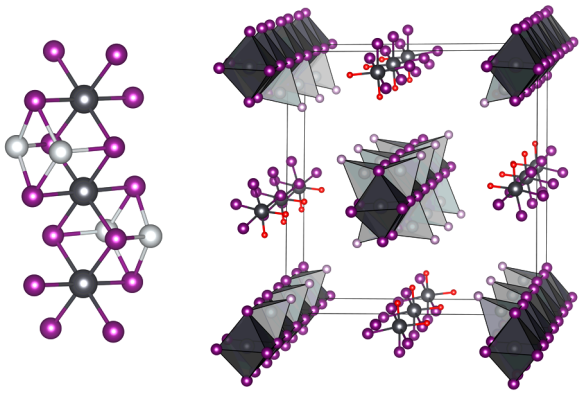


Figure 12 The novel silver iodoplumbate cubane system (left) as shown with grey polyhedra from the crystal structure of Fan *et al.*[110] The organic bridging ligands have been excluded for clarity.

Of the multitude of infrequent geometric arrangements, the di-metallic cubic system (isostructural to that of cubane) is frequently observed. Multiple publications have depicted examples of such motifs, where cube-like systems are formed from metalohalides (Figure 12).[110, 130-132] The drawbacks of designing systems based on the cubic structure is that they are 'closed systems' or tend to be 0 dimensional; the bonding does not permutate through space. Vega and Saillard suggests an example of such copper based 0D clustered systems, with band gaps ranging from 1.67 eV to 3.68 eV (dependent on ligand selection).[130] Fan *et al.* show one of the less common 2D 'cubane' structures which permeates in one direction (shown in Figure 12, repeating cube structure truncated on the left).[110]

There is extensive variability in electronic properties of these 2D hybrids. If the band-gap is the only property being tuned by the selection of metals, then it should be apparent that the local geometries are of very little significance. Any dimensionality, and any of the metals described herein, can be used as a starting block. *This illuminates the most important issue when designing electro-active frameworks: what is the role of the ligand, and how does it control electronic and optical properties?*

Metal Selection. The majority of hybrid materials are designed such that the electrons involved in conduction, excitation and chemi-luminescence originate in the valence bands of the metal.[99] In semiconductor physics, adjusting the band-gap has traditionally been achieved by doping or alloying. Whilst not as trivial as a mononuclear system such as Si, hybrids can be doped in two ways: by altering the composition of the metals, or by changing the ligands. This section will give a brief overview of the general classes, and also identify particularly interesting applications of novel ligands.

Control of metal composition is straightforward in principle but difficult in practice. There are a handful of examples of highly ordered mixed metal systems.[109, 110, 122, 133] Loye *et al.* demonstrated that a mixed metal approach did alter the band gap, but only to an average value between the two metals.[109] This particular mixed Cu/Pb compound suggested a theoretical band gap of 2.52 eV, compared to CuI (2.92 eV) and PbI_2 (2.30 eV). Mishra *et al.* demonstrated that the effect of differing quantities of both Y and Pb in the $[Y(DMSO)_jPb_kI_l]$ system had a direct variability of ~0.8 eV.[122] As

mentioned, some creativity can be applied when designing such systems. It is noteworthy that Li *et al.* have been concerned with the metal selection, and have performed computation of the electronic band structures on iodoplumbates, using density functional theory.[134] Often, selection of metals and ligands that form interesting systems in segregation can be amalgamated. A prototypical example of blending ZnSe and SnSe, both good semiconductors, is described by Philippidis *et al.* and is an important approach to tailoring the properties of such compounds.[127]

Ligand Selection. The other alternative for doping in hybrids is to manipulate the ligands. There are vast amounts of research invested in designing such ligands, as has been discussed earlier, and here we will give a collective summary of the various approaches to organic molecule selection in framework structures.

The simplest and most frequently studied ligands are the halides. By definition these are not organic, but should be discussed as the organic components are not necessarily the chemically active ligand, but the solvent, or merely occupy space (geometric/structural). A prototypical example are iodoplumbate systems, which have been reported to have variable band gaps ranging from 2.2 eV to 4.0 eV.[108, 111] There have been investigations into the electronic effects of the choice of halide. In principle, the larger the halide, the smaller the band gap due to the lower binding energy of the valence states and further relativistic effects (i.e. spin-orbit coupling). Calabrese *et al.* confirmed this rationale by demonstrating a significant decrease in band gap when substituting smaller halides for progressively larger analogues.[111] Both Kojima and Vega identified a disparity, with a band gap increase of ~0.65 eV when substituting iodide for bromide.[108, 130] This counter-intuitive result is perplexing, and demonstrates one of the limitations in theoretically designing hybrids. Unfortunately the perplexities do not end with halides, but extend to the chalcogens, pnictogens and even ammonia derivatives. It appears that pure electronic or molecular orbital arguments fail in their quantitative description due to the intimate relationship with the local structure.

Chalcogenide systems are often found in bimolecular structures (*e.g*. SnS, CdSe, ZnTe). The familiar bonding associated with chalcogens in organic chemistry gives scope for applications by terminating organic ligands with such species. For instance, Turner *et al.* have described a system where benzene hexathiolate is used in coordination with lead to form an elegant structure previously displayed in Figure 11.[106] Zhang highlights that the increase in chalcogen size decreases the band gap,

similar to what was expected for halides.[135] To the best of our knowledge, there is no current evidence to suggest the opposite trend, and hence when designing hybrids, a substitution of a larger chalcogenide will subsequently decrease the band-gap.

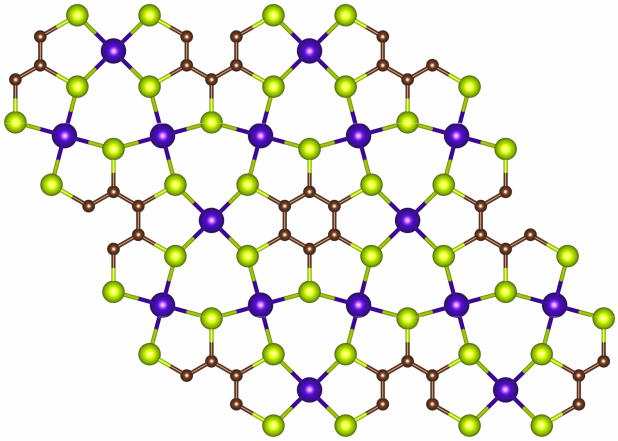


Figure 13 Predicted crystal structure of $Hg(C_6Te_6)$, following geometry relaxation at the PBEsol level of theory. The system is locally stable, adopting the same geometry as the rest of the hybrids of this class. Hg, C and Te are depicted in purple, brown and green.

It is, however, easy to forget that the end product needs to *synthetically viable*. Initial studies of analogous structures to that used in our earlier PbS hybrid work have investigated the use of benzene hexatelluride, shown in Figure 13.[136] The structure is implausible as a starting material, despite being computationally 'stable'. Hexa-substituted benzene is a synthetic challenge, and it is for this reason that sulfur and oxygen have dominated organic ligand development. Synthetically, thiols and alcohols are usually in their free acid form, and only coordinate after deprotonation. One should bear in mind that both the halide and pnictogenide variants do not require deprotonation.

Pnictogen based ligands have traditionally been used to determine the extent of branching and 3D growth, by occupying sites preventing perpetuation of bonding. Vega demonstrates how ammonia and phosphane truncate the growth of their copper cubane systems.[130] The paper also details a direct comparison of the electronic affects as a result of substituting PH_3 for NH_3. Surprisingly, NH_3 produces consistently smaller band-gaps ranging from 0.86 – 1.79 eV less than the direct phosphane analogue.

Other common pnictogen containing ligands are the variety of larger amines and diamines. Longer chain primary amines are analogous to surfactants; the amine coordinates to the metal, and the organic chain is used to create separation in the layers

of the system. Calabrese illustrates the affect of such ligands, and their applications in separating the layers in their perovskite structure.[111] Aliphatic hydrocarbons are majorly inert and highly insulating, and as such, they play little more than the role of a geometric spacer.[99] Diamines are more chemically interesting because of their role as a linking ligand in multidimensional systems. Amalgamating the rationale for the electronic properties of NH_3 and PH_3, and how aliphatic organics have little role in these systems, it is obvious that polydentate ligands of this class are again purely structural. The only differences being that these ligands dictate the dimensionality of the system.[129, 137]

The final class of organic components is the conjugated and aromatic systems. In a broad sense this embodies halides, chalcogenides, and pnictogenides, but differs by the addition of π electrons. Returning to examples from our recent work, benzene hexathiolate poses interesting implications, because it forms highly overlapped structures whilst being self-assembling.[112] In that instance the system is fully substituted, however envisaging progressively more hydrogenated systems, the substitution location becomes important. The aromatic organic components are inherently semiconductors themselves, which seemingly make them an excellent choice in designing hybrid semiconductors.[138] They also have the added benefit of inherent rigidity, promoting the self-assembly of designer systems. An interesting example of such systems is highlighted by the use of triphenylphosphane. It is both a space occupying and conductive ligand, and has been used extensively in recent publications.[110, 130] Another prototypical example is described by Holden, such that the aromatic rings are displaced from the metals, similar to those of the aliphatic amines.[97] Within this subcategory, there are so many variables in designing aromatic and conjugated hybrids that their affect is difficult to identify. Our future work aims to target a methodological approach to design hybrids materials, and this is one of the many unclear areas that should be prioritised.

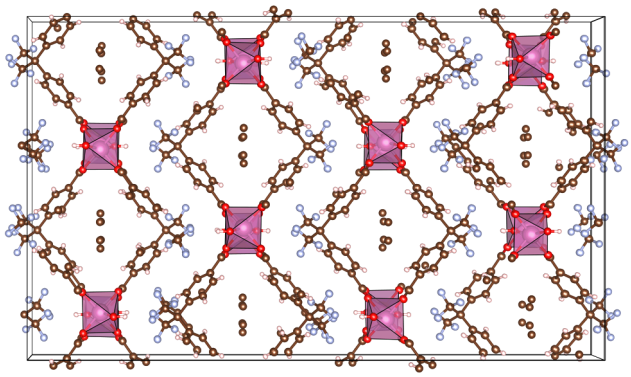


Figure 14 Indium oxide (pink octahedra) linked by a tetrahedral centered ligand, 4,4'-(hexafluoroisopropylidene)bis(benzoic acid) [H_2hippb].[139]

From the many possibilities of organic ligands, there are a few surprising examples that may be worth pursuing further. To our knowledge, Gándara *et al.* are the only group to have investigated novel 2D hybrids based on a tetrahedral carbon centered ligand shown in Figure 14.[139] The authors excluded conductivity data (both theoretical and experimental) from their report, giving little indication to their importance in semiconducting behaviour. Regardless, novel tetrahedral systems are of interest as they have poorly characterised structural motifs. We are investigating the significance of ligands of similar structure and their influence in related hybrids. The ligand described in Figure 14 is particularly interesting because it encompasses extremely hydrophobic regions (CF_3 and phenyl moieties), whilst achieving highly ordered and predictable structures. Two other noteworthy structures are described by Li and Philippidis (Figure 15). Whilst neither are entirely novel, they are representative of a larger class of organic compounds. The former tetrazol is a common structure in medicinal chemistry, and are synthetically viable. They coordinate in an interesting manner, with a backbone twist through the conjugated motifs (better described by Figure 15). This may give rise to chiral control of structural ligands, an area that is emerging and has significant implications in self-assembly and MOF design. Philippidis suggests the use of a cationic species as it not only forms a layer of repulsion between the sheets, but also acts as the counter ion in the system.[127] The example described is fully saturated, and as explored earlier, aliphatic (saturated) hydrocarbons add little electronically. One possible extension of this could be pyridinium-based ligands, but there has been no development in this area to date.

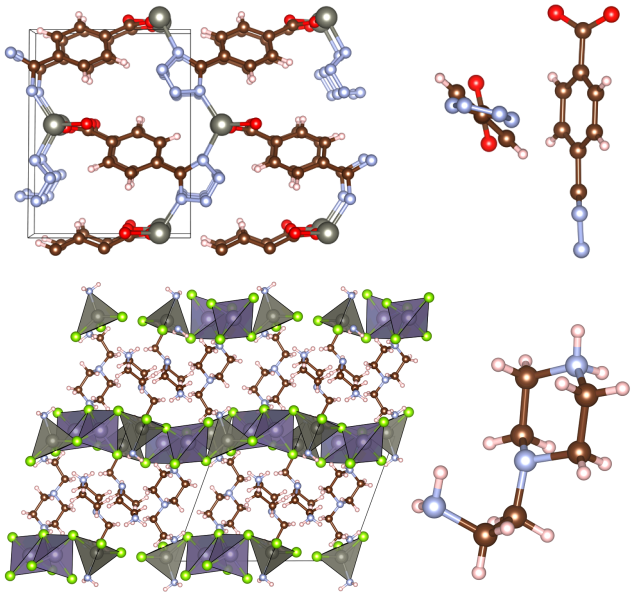


Figure 15 The crystal structure of 4-tetrazol benzoic acid depicted coordinating via 1,4 nitrogens to zinc (top left), with the nonplanar backbone twist depicted (top right).[140] Zinc tin selenide (grey tetrahedral, bottom left) linked by the novel ionic ligand, *N*-(2-aminoethyl)piperazinium (bottom right).[127]

3D Porous Metal Organic Frameworks

Porous 3D frameworks have increasing popularity as they have applications as molecular sieves, catalysts and as ion sensors. Evidently, construction of 3D hybrids for applications in optoelectronic devices is still in its infancy; however, the same concepts for metal and ligand selection discussed in the previous sections are still applicable here. A wide variety of 3D coordination polymers have been synthesized, with a few (mainly containing Cu or Ag) that exhibit low but measurable conductivities in the range 10^{-9} to 10^{-3} Scm^{-1}.[49]

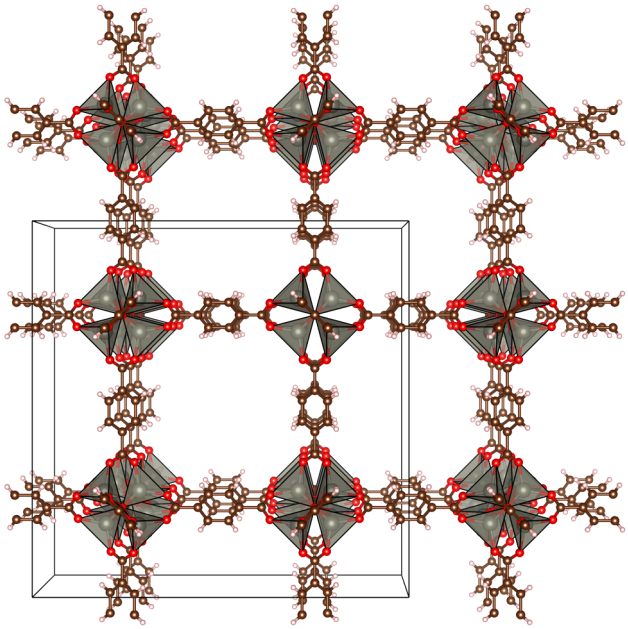


Figure 16 The crystal structure of MOF-5, with zinc oxide tetrahedra shown in grey.[141]

Of the multitude of MOFs that exist in the literature, the most notable "semiconductor" is the first isorecticular metal organic framework, MOF-5 (Zn_4O(1,4-dicarboxylate)$_3$).[141-143] The system has a distinctive cubic shape, is highly porous, and depending on bridging ligand, tunable band gaps. A band gap of ~3.5 eV has been reported for the structure shown in Figure 16.[144] Yang *et al.* proposes a similar band gap of 3.4 eV, calculated using the familiar PBE[145] density functional.[146] Other work suggests that electronic transitions are a product of O^-–Zn^+ ligand to metal charge transfer transition, fundamentally unrelated to the organic ligand.[147] Despite being lauded as a semiconductor, this assignment has been based on the photocatalytic and electrochemical response of MOF-5, and not through direct electrical measurements.[148, 149] To our knowledge, no solid-state conductivity measurements of MOF-5 have been reported to date. The calculated band structure is shown in Figure 17. Due to the large crystallographic unit cell, and the strong localization of the electron wavefunction, no appreciable band dispersion can be observed, which would be consistent with localized carriers and low levels of conductivity.

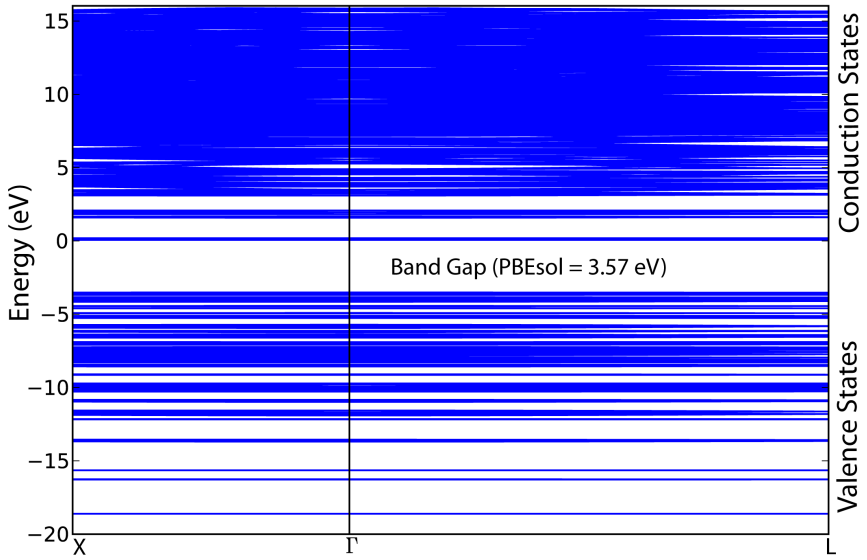


Figure 17 Calculated electronic band structure of MOF-5, using the PBEsol density functional. The x-axis relates to the direction in reciprocal space, where **Γ** lies at the centre of the first Brillouin zone.

Chen *et al.* reported MOF-76b, a terbium centered cubic system with exceptional fluoride sensing capabilities.[150] Whilst not distinctly measured in the paper, the band gap were extrapolated from the excitation spectrum and found to be approximately 3.4 eV. Conductivity measurements have been performed for a Cu-based thiophene framework ($Cu[Cu(pdt)_2]$, where pdt = pyrazine-2,3-dithiolate), which approaches 10^{-3} Scm^{-1} at room temperature,[151] while the mixed metal Cu/Ni thiophene gave similar performance.[152]

As well as promising semiconductor properties, the porous nature of many of the 3D frameworks open up the possibility for (photo)electrochemistry by filling the empty channels by a redox electrolyte. For example, Halls et al. demonstrated reversible oxidation of ferrocene using Zn(II) and Al(III) dicarboxylate frameworks,[153] and water oxidation using the Fe based Basolite MOF.[154] An even more striking example is the discovery of photochromism in a framework material based on ocatmeric TiO_2 centers, shown in Figure 18.[155] An explanation for the white-to-black colour change on excitation under UV light has been provided on the basis of electronic structure calculations:[103] band gap excitations in the material have sufficient energy to drive oxygen from the system, resulting in oxygen sub-stoichiometry compensated by a reversible reduction of Ti(IV) to photo-active Ti(III) centres. Here, the porous structure itself plays an important role in facilitating rapid ion and electron transport.

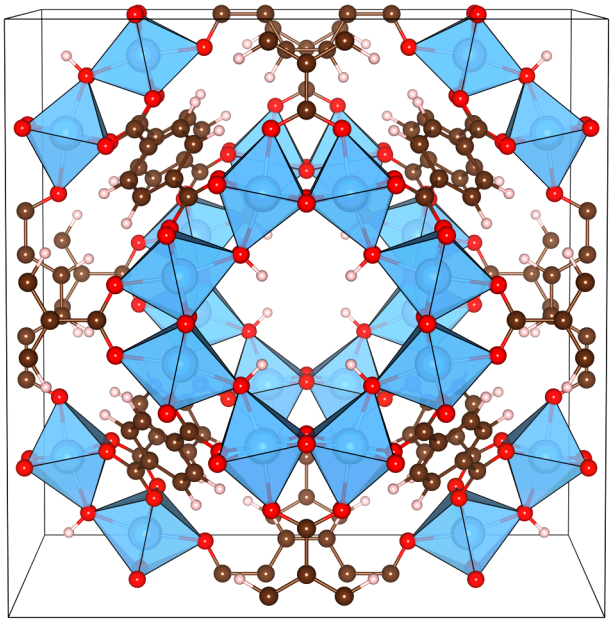


Figure 18 Tetragonal crystal structure of a TiO_2 based dicarboxylate framework material,[155] which undergoes a colour change from white to black under UV irradiation owing to chemical reduction from Ti(IV) to Ti(III).[103]

Conclusions and Challenges

We have attempted to provide a succinct account of the current status of research into hybrid semiconductors. While there has been great progress towards the development of 1D, 2D and 3D systems that absorb light and conduct electricity, there is thus far no evidence demonstrating direct applications in high-efficiency photochemical or electrochemical devices.

We have highlighted a number of areas of deficient methodology in designing hybrid framework materials, including the significance of atomic radii in determining the topology; the influence of conjugation and the application of designer ligands to tune both photochemical and structural properties.

In tuning the properties of these materials, it is clear that the metals and ligands, as well as their long-range order, will each play a critical role. One of the grand challenges is to elucidate the structure-property-composition relationships in these systems, to provide a transparent set of design principles. We are current developing a computational procedure to develop a thorough understanding of:

- electronic communication between organic and inorganic building blocks;
- guidelines for the choice of metals and ligands to achieve desired properties;
- strategies for doping to control electron and hole concentrations.

Our preliminary results suggest that this is a promising route to pursue.[104] Given the size and complexity of the crystal structures of hybrid framework materials, these systems represent a significant task for contemporary materials modelling. However, taking into account the recent success of high-performance computing in the chemistry and physics of materials,[156] it is a feasible one. Following the device roadmap set out by Allendorf *et al.* for the exploitation of conductive MOFs in devices, an understanding of the fundamental properties will soon be followed by thin film growth; multi-level structures; device integration and finally manufacturing.[157]

Given the recent advent of mobile electrons in cement, which was once considered to be chemically inert,[158] the future for electrons in metal organic frameworks looks promising.

Acknowledgements

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